

Charge-Discharge Characteristics Improvement Through Optimization of Voltage Range for LiNiCoMnO₂ Electrode for High Energy Density Lithium-Ion Batteries

(Penambahbaikan Ciri-ciri Cas-Nyahcas Elektrod LiNiCoMnO₂ Melalui Pengoptimuman Julat Voltan untuk Bateri Ion Litium Berketumpatan Tenaga Tinggi)

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ABSTRACT

The development of suitable electrode materials for lithium ion batteries (LIBs) to enhance the performance of LIBs in order to meet increasingly demand globally is one of the challenges. Thus, for almost three decades since 1980, continuous study for high performance LIBs electrode has been done. In this report, the optimization charge-discharge characteristic of LiNiCoMnO₂ (LNCM) cathode – layered structured material with lithium metal as anode has been evaluated. The electrode was assembled together with Celgard as separator and organic electrolyte Lithium hexafluorophosphate (1M LiPF₆, EC:DEC 1:1) in coin cells (CR2032) under argon atmosphere inside a glove box. The charge-discharge performance test was conducted using Neware battery testing system. The discussion in this paper is focusing on the characteristic features of the charge-discharge profile, optimize charge-end voltage and rate capability (C-rate). The studies discovered the voltage range has been optimized up to 3.3-4.5 V at a constant current of 0.35 mA (0.1 C) with voltage plateau of 4.0 V. The result indicated the optimized range has the highest specific capacity of 118 mAh/g and most stable coulombic efficiency (94.3%).

Keywords: Battery; Charge-discharge; Lithium-ion; LiNiCoMnO₂; power capacity

ABSTRAK

Pembangunan bahan elektrod yang sesuai untuk bateri litium ion (LIBs) bagi meningkatkan prestasi LIBs untuk memenuhi permintaan yang semakin meningkat di peringkat global adalah salah satu cabaran. Oleh itu, hampir tiga dekad sejak tahun 1980 banyak penyelidik melakukan kajian berterusan untuk meningkatkan prestasi elektrod LIBs telah dilakukan. Dalam laporan ini, ciri-ciri cas-nyahcas yang disyorkan daripada bahan berstruktur berlapis katod LiNiCoMnO₂ (LNCM) dengan anod litium untuk bateri ion litium dinilai. Elektrod dipasang bersama pemisah Celgard dan elektrolit organik litium heksafluorofosfat (1M LiPF₆, EC:DEC 1:1) dalam sel koin (CR2032) di bawah atmosfera argon di dalam kotak sarung tangan. Ujian prestasi cas-nyahcas dijalankan dengan sistem penguji bateri Neware. Perbincangan dalam manuskrip ini memfokuskan kepada pencirian ciri-ciri cas-nyahcas, mengoptimumkan voltan cas-akhir dan keupayaan kadar (kadar-C). Kajian mendapati rangkaian voltan telah dioptimumkan sehingga 3.3-4.5 V pada arus malar 0.35 mA (0.1 C) dengan voltan penara 4.0 V. Hasilnya menunjukkan julat yang dioptimumkan mempunyai kapasiti spesifik tertinggi 118 mAh/g dan kecekapan kuolom yang paling stabil (94.3%).

Kata kunci: Bateri; Cas-nyahcas; Litium-ion; LiNiCoMnO₂; kapasiti kuasa

INTRODUCTION

Lithium-ion batteries (LIBs) have been regarded as 'Holy Grail' of battery and advanced technology since its first commercial production by Sony for past three decades. It is commonly used as energy storage in mobile phone, laptop, portable electronic devices and up to vehicle purposes. Recently, LIBs have shifted its focus on development and commercialization of larger battery for hybrid electric vehicles (HEVs) and electric vehicles (EVs). LIBs have become the main interests for researchers and industries due to its higher energy density, lower self-discharge and longer life

cycle performance compared with other batteries such as nickel cadmium (NiCd) and nickel metal hydride (NiMH) batteries. Through extensive research, various promising electrodes with different structures have been created. For example, lithium cobalt oxide (LiCoO₂ or LCO) – layered structure, lithium manganese oxide (LiMn₂O₄ or LMO) – spinel's structure and lithium iron phosphate (LiFePO₄ or LFP) – olivine structure, to name a few (Julien et al. 2014; Yi et al. 2016). All these LIBs compound materials are broadly used for study to achieve better life cycle with high rate capacity and rigorous safety. However, these electrodes is far from perfect. The LCO has become less popular choice due to

its high price of cobalt (Co), Co is rare earth material and is toxic even though it has good specific energy (150-200 Wh/kg); LMO has shorter life cycle (300-700 cycles) although it can achieve higher voltage (nominal voltage of 3.80 V); whilst LFP which has been determined as best candidate so far due to safety reliability but come with a cause of lower capacity and voltage (Armstrong and Bruce 1996; Fergus 2010; Kim et al. 2015; Nitta et al. 2015). Moreover, due to the demand from the global industries and various parties to achieve a sustainable green and environmental friendly battery, many comprehensively research have been done to find alternative and the best choices for LIBs. As the above mentioned compounds were positive electrode material (cathode), with the aim of to find the best choices of LIBs must have properties such as large rechargeable capacity, high operating voltage and high-energy densities so as to have optimize LIBs (Yi et al. 2016; Zhang et al. 2015). Even though LMO is a promising cathode because it is cheaper and less toxic compare to LCO, it suffered capacity fading during cycling due to the dissolution of manganese (Mn) due to hydrogen fluoride (HF). The HF is produce during the reaction of LiPF_6 and H_2O , especially at elevated temperature. Therefore, LMO was found not suitable for electric vehicle because larger batterie were used and this caused higher operating temperature which required a cooling system. In order to improve the LMO electrochemical properties, nickel (Ni) and Co, were introduced to enhance the capacity and prolong the life span leading better energy storage performance. This electrode is known as lithium nickel manganese (LiNiMnCoO_2 or NMC). These combinations of three active materials of Ni, Mn and Co with Li brings out the best in each system, to equip a wide range of applications for automotive and energy storage systems (EES) that call for frequent cycling. This was discovered by (Nitta et al. 2015)

with existence of Ni enable to help a greater extraction of Li capacity, while addition of Mn and Co are able to enhance cycle life and safety. Furthermore, the NCM is preferred for upmost electric vehicles, such as the Chevy Volt, Nissan Leaf and BMWi3 due to push performance and extended driving range. The summary of the LIBs characteristic is tabularizing as follows in Table 1. Thus, in this paper we reported the performance of NMC as future alternative to LCO and LFP for high power energy storage application. This paper also discussed on the characteristic features of charge-discharge profile, optimize charge-end voltage as well as discharge limit voltage with a different charging/discharging rate. These initial works and results will be used for further study on BMS optimization.

METHODOLOGY

MATERIALS

Commercial grade electrode materials use is LiNiCoMnO_2 ($d=1.25$ cm), Celgard 2300 with thickness $25\text{ }\mu\text{m}$ (porous polypropylene membrane), coin cells CR2032 casing with stainless steel spacer (0.5 mm) and spring obtained from KGC Resources Sdn. Bhd., Selangor Malaysia. While, Li metal ($d=1.6$ cm), organic electrolyte, which was 1.0 M lithium hexafluorophosphate (LiPF_6) in a 1:1 volume/volume (v/v) of ethylene carbonate (EC):diethyl carbonate (DEC) mixture – impurities < 15 ppm H_2O , 50 ppm HF with colour APHA < 50, density 1.26 g/mL purchased from Sigma Aldrich, Japan (high purity Li battery grade, Mitsubishi chemical company), whereas all materials used without further purification except electrode and Celgard were dried at 80°C for 24 hours.

TABLE 1. Characteristics of LIBs

Compound (Framework)	Specific capacity (mAh/g)	Working range (V)	Average potential (V vs. Li^+/Li)	Cycles (n)	Cost	Safety	References
LiFePO_4 (Olivine)	170/170 ^a	2.0-4.0 ^c	3.4/3.45 ^a	1000-2000	Average	Excellent	Nitta et al. 2015
LiMn_2O_4 (Spinel)	148/148 ^a	3.0-4.5	4.1/4.1 ^a	300-700	Low	Good	Nitta et al. 2015
LiNiCoMnO_2 (Layered)	280/272 ^a	2.0-4.4 ^b	3.7/4.0 ^a	1000-2000	Average	Good	Nitta et al. 2015

Sources: ^{a,c} Julien et al. 2014, ^b Dou 2013

FABRICATION

Half-cell battery was constructed in a glove box with full of dry argon gas atmosphere (1.0 ppm O_2 and 0.1 ppm H_2O). The coin cells were fabricated using the Li metal as anode, LiNiCoMnO_2 as cathode, Celgard as a battery separator and electrolyte used was organic electrolyte (1M LiPF_6 , EC:DEC 1:1 v/v). All experiments were carried out at room temperature (25°C).

CHARACTERIZATION

Prior to battery testing, the coin cell batteries were put to rest over night to allow the potential stabilize. The long

open-circuit relaxation time is to ensure an equilibrium open-circuit potential by examine the OCV value using multimeter. Charging-discharging of the cell were realized by setting the voltage range of the electrode materials respectively as shows in Table 2 and Table 3. All potentials given are versus the Li/Li^+ reference electrode in the organic electrolyte, (1M LiPF_6 , EC:DEC 1:1 v/v). Charge (Li intercalation) and discharge (Li deintercalation) characteristics were measured between +2.6 to +4.8 V at a constant current with determined current rates (C-rate) between 0.1, 0.3, 0.5 and 1.0 C. The charge and discharge performance test was conducted with 5 V 10 mA NEWARE battery testing system (BTS 3000 type) at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the initial charge-discharge profiles and cyclic performance of the samples S1, S2 and S3 at 0.1 C under various cut-off voltages. The samples present the initial discharge capacity of 74.3, 86.8 and 188.0 mAh/g under the upper cut-off voltage 4.2, 4.2 and 4.5 V, respectively. Open circuit voltage of freshly fabricated cells is determined at 3.0 V. S3 charge and discharge curves obtained with the

setting the charge-end voltage of 4.5 V and discharge limit voltage of 3.3 V. Initially, the voltage of sample S3 start off at 3.9 V. The profile discharge curve presented a practical capacity of 118 mAh/g while the charging curve indicating practical capacity of 125 mAh/g out of 155 mAh/g base on theoretical capacity of manufacturer (KGC Resources Sdn. Bhd.). Previous researches discovered are 4.12 V (Yabuuchi et al. 2007), 3.85 V (Yoshizawa & Ohzuku 2007) and 3.7 V (Nitta et al. 2015), respectively.

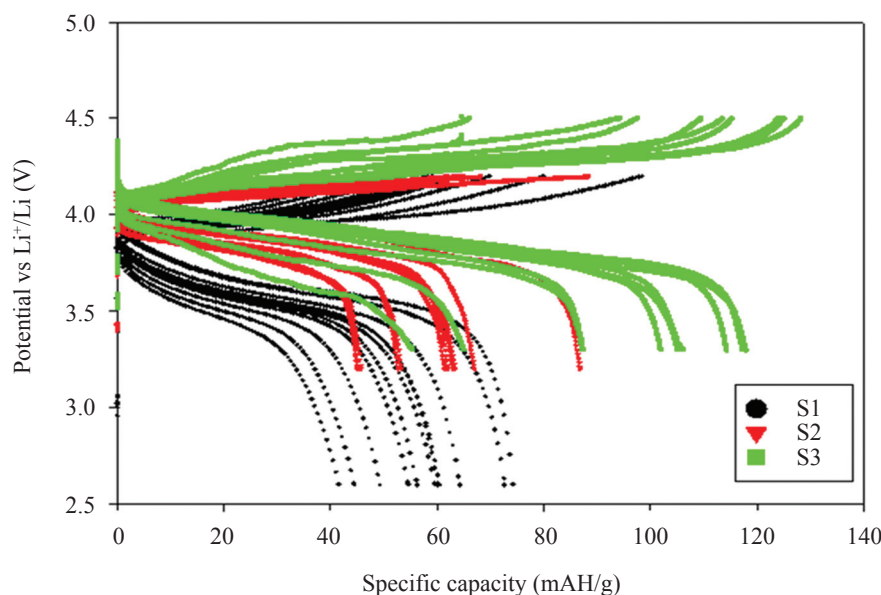


FIGURE 1. Charge-discharge profiles of LiNiCoMnO₂/Li cells at 0.1 C-rate and $I = 0.35$ mA operated in voltage ranges of (a) S1 – 4.2/2.6 V, (b) S2 – 4.2/3.2 V, and (c) S3 – 4.5/3.3 V, for initial 10 cycles respectively

TABLE 2. LiNiCoMnO₂/LiPF₆ (1M) in EC:DEC (1:1 v/v)/Li at 0.1 C

Samples	OCV (V)	I (mA), C-rate (0.1 C)	Charge-Discharge (V)	Average voltage (V)	Specific Capacity (mAh/g) by experiment	Coulombic Efficiency (%)
S1	2.7	0.4	2.6-4.2	3.9	74.3	90.8
S2	3.0	0.4	3.2-4.2	3.9	86.8	99.9
S3	3.0	0.4	3.3-4.5	4.0	118.0	94.3

Therefore, this result with potential limits between 3.3 and 4.5 V at rate of 0.1 C setting was determined as acceptable new working range and is able to become a benchmark for better performance of the electrochemistry in the cell of LiNiCoMnO₂ as a cathode. In real practical situation, the capacity is often less than theoretical capacity due to that of the Li⁺ ions cannot be removed entirely from the lattice of the host material. Meanwhile, the state-of-charge (SOC) at 0% and 100% is of the instances of empty and full charge states of a battery. Previous studies by Yabuuchi et al. (2007) shows varies cells operated in voltages of 2.5 to 4.2, 4.3, 4.4, 4.5, 4.6, or 4.7 V of charge-end voltage at 30°C (Yabuuchi et al. 2007). In addition, capacity fades when charge-end voltage was found at 4.7 V at 0.15 mAh/cm². In order to develop a long-life Li-ion battery, they suggests a charge-end voltage need to be lower than 4.4 V. This is important to avoid the occurrence of capacity fading during cycling due to change in lattice volume.

The initial charge-discharge profiles and cycle performance under various C-rates are presented in Figure 2. When the battery is charged at the constant current of discharge process, the capacity is decreased along with the increased current rate. For example, the sample S4, S5, and S6 shows the discharge capacity of 114.9, 98.6 and 55.4 mAh/g at 0.3, 0.5 and 1.0 C, under the upper cut-off voltage 4.8, 4.6 and 4.8 V, respectively. It shows that mainly the discharge capacity is recognized relatively on the much volume of charge capacity has. A good performance cells was indicated by good specific capacity of the cells whereby it can perform more lithium ions (Li⁺) extraction, in which will result more Li⁺ are reinserted during redox process. Moreover, under a fast discharging process may incurred reason for some Li⁺ cannot be reinserted to the electrode. As an example, the sample S3 and S6 presents discharge capacity of 118 and 55.4 mAh/g at charged under 0.1 and 1.0 C rates, respectively.

For the sample S4, the absolute value of charge/discharge current was increased to 0.3 C from 0.1 C. The setting of working voltage range was applied from 3.3 V to 4.8 V. From the curve, capacity was decreased. Thus, when the C-rate is increased 0.3 C, charging curve (S4) profile indicated not well finish, and NCM potential seems can go higher than the 4.8 V if compare to S1, S2, S3 at C-rate 0.1 C.

As can be seen clearly in Figure 2, the profile result of S5 and S6, is not doing well compare to S3 and S4. When the charge end voltage reduced by 0.2 become 4.6 V, the charging specific capacity S5 was decreased to 114.8 mAh/g at the C-rate 0.5 C with a constant current 1.42 mA, compare to 150.3 mAh/g of sample S4 (0.3 C). It supposed to a discharge capacity increased when higher charge-end voltage applied to the cells, as was already determined (Yabuuchi et al. 2007). Therefore, the result of sample S5 shown that rechargeable capacity is not a function of charge-end voltage, despite of the charge-discharge curve profile not well perform.

Figure 2 also shows the charge-discharge profiles of the sample S6 under the cut-off voltage of 4.8/3.3 V with a constant current 2.56 mA. The samples show a very much less discharge capacity 55.4 mAh/g at C-rate 1.0 C amongst other samples. A big gap was predicted that may cause of low valence transition for metal cations (Ni^{+}) and low strain, low concentration which cause of low rechargeable capacity in

layered cathodes (Scrosati & Garche 2010) even at higher rate of 1.0 C compare to S1, S2, S3, S4 and S5. Anyhow many possibilities can cause of fading cells due to electrochemistry of the cell. The capacity fading at higher rate can be related to pseudocapacitive behaviour in which is mostly dominated by surface and subsurface reactions due to existence of a set of different redox sites. The importance of pseudocapacitance in batteries is during the high rate charge/discharge where the battery performance tends toward a pseudocapacitive behaviour which is represented by the diagonal charge/discharge curves instead of the characteristic flat plateaus of the batteries (Eftekhari 2017; Brousse et al. 2015).

This is clearly seen in our case whereby 0.1 C has almost flat plateau and 0.3 C has a clear diagonal curve. Moreover, a comparison of the margins of the plateau potentials was taken at different C-rate. Here the potential difference can be representing the degree of polarization of the electrode. Overall, the potential margin is getting larger when C-rate increased, which indicated that the higher charging-discharging rate has slower reaction kinetics due to the higher resistance and polarization of the electrodes. In another word, the resistance can be reduced by improving the electrical conductivity of the electrode, in this case is usually binder.

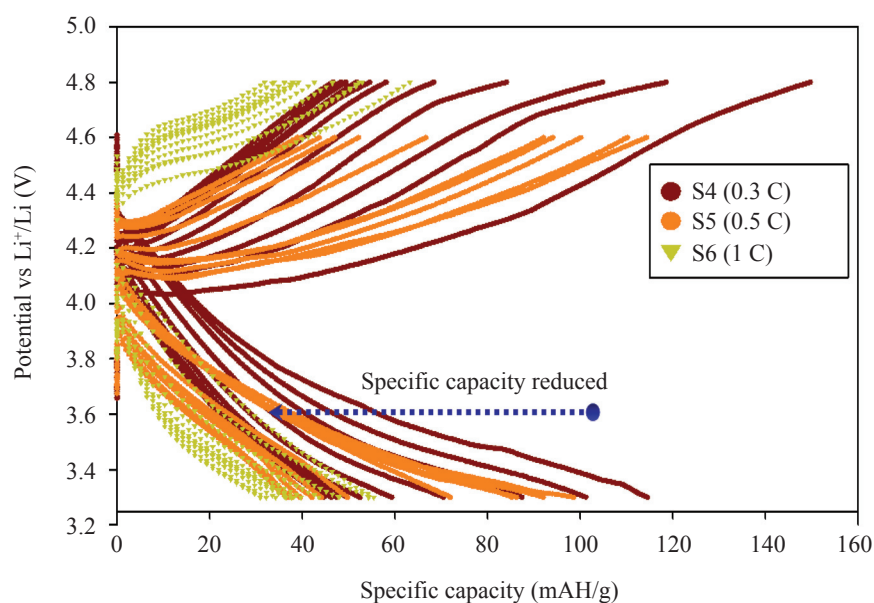


FIGURE 2. Charge-discharge curve of $\text{LiNiCoMnO}_2/\text{Li}$ cells operated at various C-rate (a) $I = 0.8 \text{ mA}$ (0.3 C), (b) $I = 1.4 \text{ mA}$ (0.5 C), (c) $I = 2.6 \text{ mA}$ (1.0 C) for initial 10 cycles respectively.

TABLE 3. $\text{LiNiCoMnO}_2/\text{LiPF}_6$ (1M) in EC:DEC (1:1 v/v)/Li

Samples	OCV (V)	I (mA), C-rate (xC)	Charge-Discharge (V)	Average voltage (V)	Specific Capacity (mAh/g) by experiment	Coulombic Efficiency (%)
S4	3.0	0.8 (0.3 C)	4.8-3.3	4.0	114.9	76.5
S5	2.8	1.4 (0.5 C)	4.6-3.3	3.4	98.6	86.2
S6	2.9	2.6 (1.0 C)	4.8-3.3	4.1	55.4	87.7

Figure 3 shows the specific capacity, cyclic performance and coulomb efficiency of NMC/Li indicated of mention samples S1-S6 at elevated C-rate initially 0.1 C incrementally to 1.0 C at the various cut-off voltages 2.6/4.2, 3.2/4.2, 3.3/4.5, 3.3/4.8 and 3.3/4.6 V at 25°C. The coulomb efficiency (CE), is actually is a method that can be outlined as the efficiency of electrons are transmitted in an electrochemical system. As shown in Figure 3, initially CE between S1, S2 and S3 presents

as 90.8, 99.9 and 94.3%, respectively. The CE normally calculated with the division of the discharge capability over the charge capacity. The higher charge capacity happens during the initial charging process, is attributed due to the extraction of Li^+ and creation of solid electrolyte interphase (SEI) film on the electrodes (anode) surface; the discharge capacity is attributed to the reinsertion of Li^+ in the following discharging process.

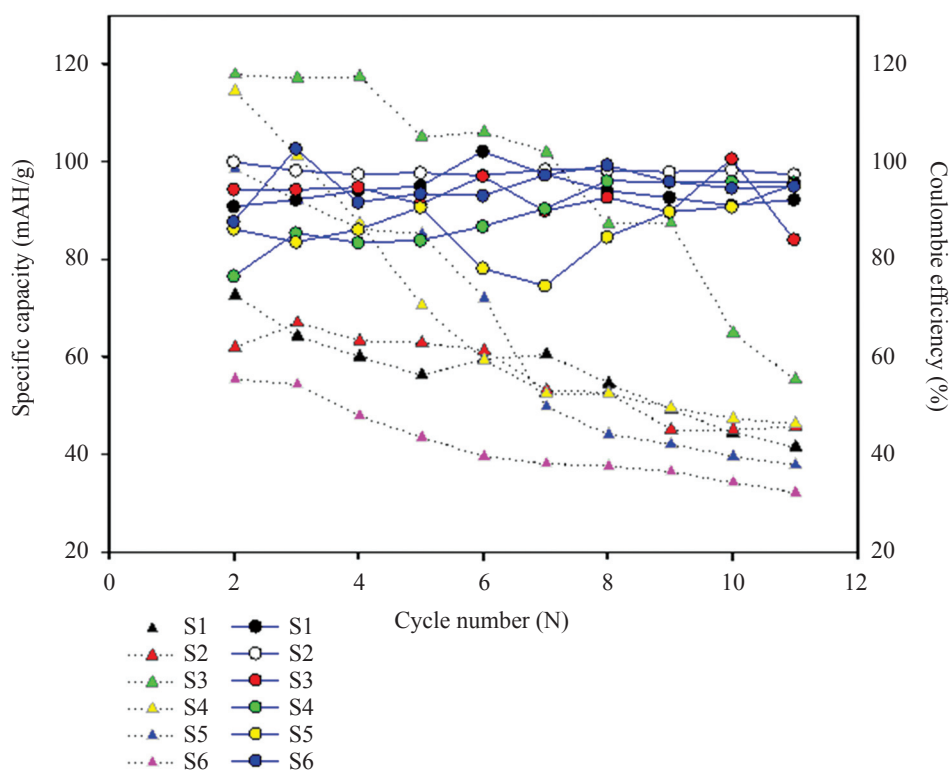


FIGURE 3. Relationship with coulombic efficiency, capacity and figure 1d cycle life performance for initial 10 cycles respectively

Therefore, by theory the CE in the first cycle has been always lower than those in the next rounds. Even though the sample S6 appears at the highest cut-off voltage of 4.8 V, but presented lowest initial discharge capacity. The discharge capacity S6 presents a relatively fast degradation, initially CE 87% at first 10 cycles. Whilst the samples S3 worked at the cut-off voltage of 4.5 V presents a good cycle performance, remaining highest capacity at first cycles onwards and CE. A high CE value can provide a longer life of NMC/Li as S3 indicated the most stable amongst of other samples.

The charge/discharge profile, cyclic performance and CE usually correlate with capacity loss of battery. Therefore, percentage of capacity loss after 10 cycles for all mention samples is varies from between 25% to 61%, giving an average capacity loss per cycle range of 2.5-6.0% per cycle as shown in Figure 3 as well. Thus, from Figure 3 also demonstrates capacity loss caused by the typical redox process during charge/discharge cycle eventually cycled at a 0.1, 0.3, 0.5 and 1.0 C. The rapid loss of capacity at higher C-rates could be Li ion attributing at the anode due to rapid charging. A moderate charge and discharge currents shall

reduce structural degradation which applies to most battery chemistries. Recent work by Jin et al. (2017), has improved the initial coulombic efficiencies from 71.74% to 84.99% (at 20 mA/g in 2-4.8 V) by introducing Co_3O_4 coating which later transforms to cubic phase of $\text{Li}_x\text{Co}_y\text{O}$ active layer during initial discharge process. The ideas combines the functions of protective layer and electrochemically active Li-free insertion host for overcome the cycling stability and low initial coulombic efficiency of Li-ion batteries.

CONCLUSION

In summary, the LiNiCoMnO_2 is one of the potential and promising lithium ion battery for high-power applications, preferences for green automotive like electric and hybrid vehicles. As for this study discovered that the voltage range has been optimized at 3.3-4.5 V and includes voltage plateau at 4.0 V as shown in S3 which new pointed out. The cell was cycled at a constant current of 0.35 mA (0.1 C) between potential limits 3.3 and 4.5 V, and indicated the most stable amongst of other samples. Nevertheless, as enhancement to

Li-ion battery is needed continuously to lift up performance, and the research is still open to find better electrode (cathode and anode) which is not only excellent on high-power application but longer cycle life, economical and safety.

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